# ESR–thermoluminescence correlation studies of sodium and lithium diborate compounds

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**Abstract.** Gamma-irradiated sodium and lithium diborate compounds have both paramagnetic and thermoluminescent centres. ESR–TL correlation measurements indicate that the paramagnetic centres can only be related to the thermoluminescent processes taking place at temperatures higher than 150 °C when the heating rate is equal to or greater than 2 °C min$^{-1}$.

## 1. Introduction

Paramagnetic centres in $\gamma$-irradiated $(M_2O)_x(B_2O_3)_{1-x}$ compounds and glasses, where M stands for an alkali metal, were the subject of many studies between the years 1953 and 1972 [1–7]. The ESR spectra of the compounds show hyperfine structure. Experimental evidence indicates there are two kinds of paramagnetic centres. One is a trapped hole in an oxygen atom having a hyperfine interaction with two boron atoms, as shown in figure 1(a). The other centre is believed to consist of a trapped hole in an oxygen atom having a hyperfine interaction with a boron atom. For this centre three configurations have been proposed (see figure 1(b)) [7].

In 1971, Shearer [8] investigated the thermoluminescent properties of lithium diborate glasses irradiated with 15 MeV electrons, and assumed that the paramagnetic centres induced by the electron radiation are involved in the thermoluminescent processes [8]. Later, in 1980, Nasipuri and co-workers reported on the thermoluminescent behaviour of a series of sodium diborate glasses containing different concentrations of $Na_2O$. The samples were irradiated with 30 keV x-rays [9]. In [9] it is stated that the irradiation produces paramagnetic centres. Recently we have observed that $\gamma$-radiation from a $^{60}Co$ source makes sodium and lithium diborate compounds thermoluminescent and simultaneously induces paramagnetic centres. The signals are very similar to those reported earlier in other work on sodium and lithium diborate glasses. We have made use of this result in performing ESR–TL correlation measurements to investigate whether the paramagnetic centres are involved in the thermoluminescent processes.

## 2. The ESR–TL correlation method

If free electrons or holes are not recaptured by traps, the density of trapped electrons or holes is given by
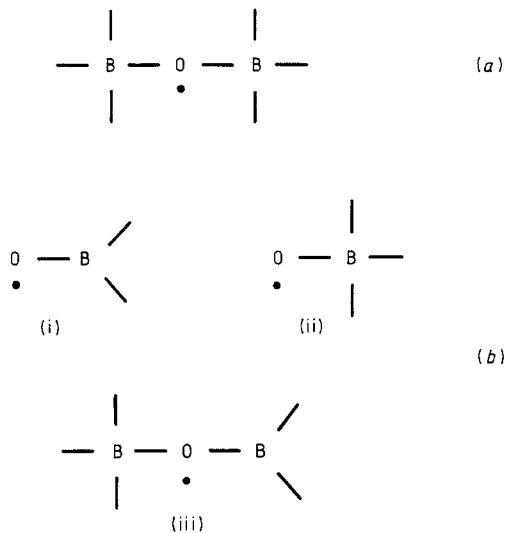
$$n = n_0 \, e^{-t/\tau} \tag{1}$$

Figure 1. Paramagnetic centres. (a) Type I: a hole on an oxygen bridging between two equivalent four-coordinated borons. (b) Type II: (i) a hole on a non-bridging oxygen on a three-coordinated boron; (ii) a hole in a non-bridging oxygen on a four-coordinated boron; (iii) a hole on a bridging oxygen between three- and four-coordinated borons.

where

$$\tau = \exp(E_T/kT)/s \tag{2}$$

and $n_0$ is the density of trapped electrons or holes at $t = 0$, $E_T$ is the trap depth, and $s$ is a frequency factor.

If a sample is subjected to step annealings at successively higher temperatures $T_j$, the ratio $r_j$ of the ESR signal intensity after the $j$th annealing step and that before the first annealing is given by

$$r_j = \exp(-s\Delta t \gamma(T_1, T_2, \ldots, T_j)) \tag{3}$$

where $\Delta t$ stands for the duration of each annealing step and $\gamma$ is given by

$$\gamma(T_1, T_2, \ldots, T_j) = \sum_{i=1}^{j} \exp\left(-\frac{E_t}{kT_i}\right). \tag{4}$$

This result is obtained by assuming that the frequency factor $s$ is slowly varying with temperature and can be considered a constant for a particular trap. It is also assumed that the decrease of the density of the trapped electrons or holes during the cooling to room temperature and heating of the sample between successive annealings is negligible (the ESR signal intensities between two successive annealings were measured at room temperature, in order to obtain a better signal-to-noise ratio). This can be ensured by choosing the annealing time in such a way that the ESR signal intensity barely differs from that corresponding to longer annealing times.

Taking typical values for $s$ ($s \simeq 10^9 \, \text{s}^{-1}$) and $E_t$ ($E_t \simeq 1$ eV), the ratios $r_j$ have been computed and the result is shown in figure 2 for annealing times ranging from 1 to 30 min. The annealing temperatures were chosen to be between 20 and 400 °C in steps of 20 °C. In the case of two traps with different trapping depths the curve shown in figure 2 is obtained. A similar behaviour is found if there is a population transfer from one trap to another. The position of the region of maximum slope in figure 2 depends on the annealing time $\Delta t$ and the annealing temperatures.

The temperature $T_m$ at which the maximum of the glow peak occurs can be computed from

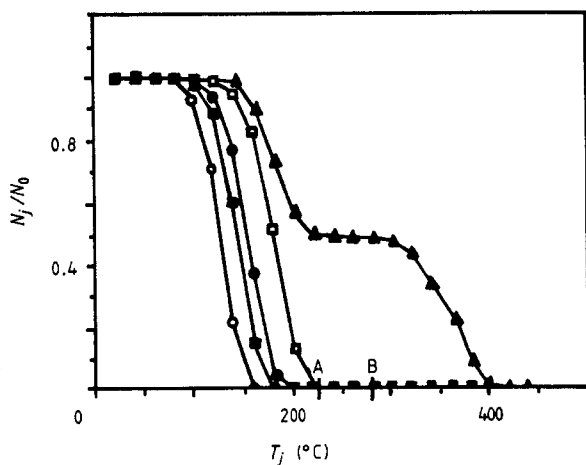$$\beta = (Sk/E_t)T_m^2 \exp(-E_t/kT_m) \tag{5}$$

**Figure 2.** The ESR signal intensity against annealing temperature. (i) When there was one trap, $s$ was taken equal to $10^9\,s^{-1}$ and the trap depth to be equal to 1 eV. Annealing times: $\square$, 1 min; $\bullet$, 5 min; $\blacksquare$, 10 min; $\bigcirc$, 30 min. The temperature $T_m$ at which the glow peak occurs for the trap is indicated in the figure for two heating rates: for $\beta = 2\,°C\,min^{-1}$ it is $T_m = 230\,°C$ (denoted by A); for $\beta = 25\,°C\,min^{-1}$ it is $T_m = 285\,°C$ (denoted by B). (ii) When there were two traps, the trap depths were taken to be equal to 1 and 1.4 eV respectively, and $s$ to be equal to $10^9\,s^{-1}$. Annealing time: $\blacktriangle$, 1 min.

where $\beta$ stands for the heating rate employed in obtaining the glow curve. Using the same values as were employed for calculating the curves plotted in figure 2 we computed the temperatures $T_m$ for two heating rates, $\beta = 2$ and $25\,°C\,min^{-1}$. These temperatures are given in the caption of figure 2 and they are higher than the temperatures at which the maximum slope occurs.

The disappearance of the ESR signals at temperatures lower than or similar to those for the peaks in the glow curve has been observed in previous work [10, 11]. It can be shown that this result is always obtained if the heating rate $\beta$ is equal to or higher than $\beta_0\,(T_j - T_{j-1})/\Delta t$, where $T_{j-1}$ and $T_j$ stand for two successive annealing temperatures and $\Delta t$ has the same meaning as in (3).

We will use this result to ascertain whether a paramagnetic centre could be connected to thermoluminescent processes related to a temperature region of the glow curve.

## 3. Results and discussion

TL glow curves have been obtained by heating the irradiated sample and recording the intensity of the emitted light with a phototube. The heating rates were 10, 50 and $250\,°C\,min^{-1}$. Figure 3 shows glow curves obtained for sodium diborate at different times after irradiation. It can be seen that the relative intensities of the peaks at about 120 and $220\,°C$ depend on the time interval between the sample irradiation and the measurement of the glow curve. It is well known that at every temperature there is a decrease in the number of thermoluminescent centres. Generally, the lower the temperature at which a peak occurs, the larger the rate of decrease. This could account for the changes in the relative intensities of the peaks observed at about 120 and $220\,°C$ for the different glow curves. As can also be seen from figure 3, the position of the first maximum is different for the glow curves shown in the figure, i.e., the longer the time between irradiation and measurement, the higher the temperature at which the maximum occurs. This indicates that the peak at about $120\,°C$ may be composed of several unresolved glow peaks or of the overlap of the peak with the shoulder of the high-temperature peak. Lithium diborate shows a similar behaviour. In figure 4 two glow curves of lithium diborate recorded 20 min and 15 days after irradiation are shown. As can be seen, after 15 days the peak at about $120\,°C$ has largely disappeared and a peak may be noticed between 180 and $280\,°C$ (heating rate $250\,°C\,min^{-1}$). This peak cannot be observed in curve A because of
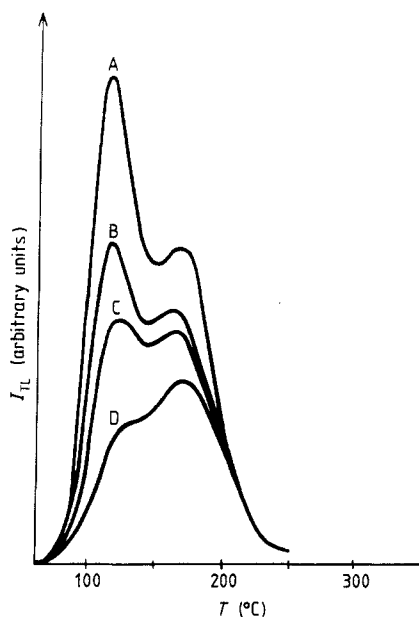
**Figure 3.** Glow curves for sodium diborate (A) 12 hours, (B) 3 days, (C) 4 days and (D) 30 days after irradiation. The intensity scale is not the same for the four spectra: the scales have been chosen so as to avoid overlap of the glow curves. Heating rate: 50 °C min$^{-1}$. Dose: 2.5 Mrad.
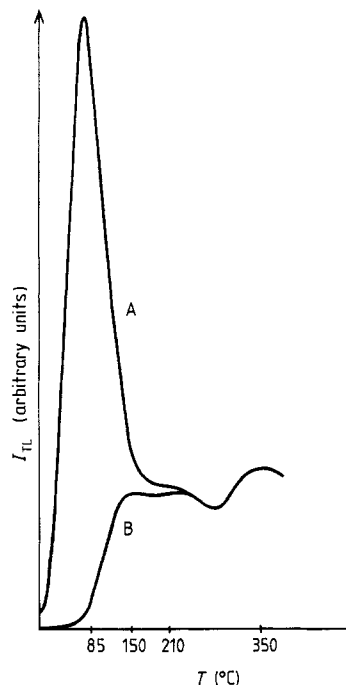
**Figure 4.** Glow curves for lithium diborate (A) 20 minutes and (B) 15 days after irradiation. Heating rate: 250 °C min$^{-1}$. Dose: 1 Mrad.

the overlap with the low-temperature peak. This result also shows that the shift of the maximum of the low-temperature peak is due mainly to the overlap with the peak at about 230 °C. Glow curves of sodium and lithium diborate compounds recorded 40 days after irradiation are plotted in figures 5 and 6. In the case of sodium diborate the glow curve consists of a broad peak ranging from 130 to 300 °C. The curve of lithium diborate shows two major peaks, i.e., a high-temperature peak at about 280 °C and a low-temperature peak. The latter is broad, due in part to the overlap with the shoulder of the high-temperature peak and possibly with the low-temperature one, if it has not completely disappeared after 40 days.
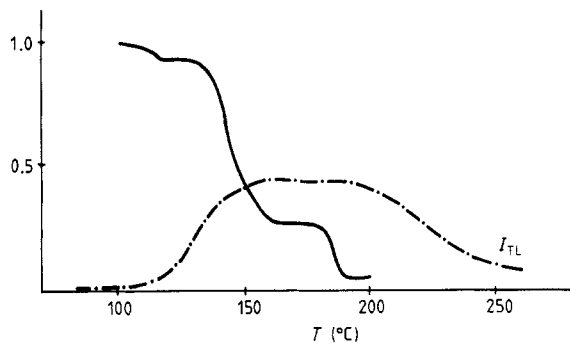


**Figure 5.** Step annealing curves for sodium diborate compounds. $I_0$ is the ESR signal intensity before the annealing steps. For the glow curve (indicated by the chain curve; arbitrary units) the heating rate was 10 °C min$^{-1}$. Dose: 4 Mrad.
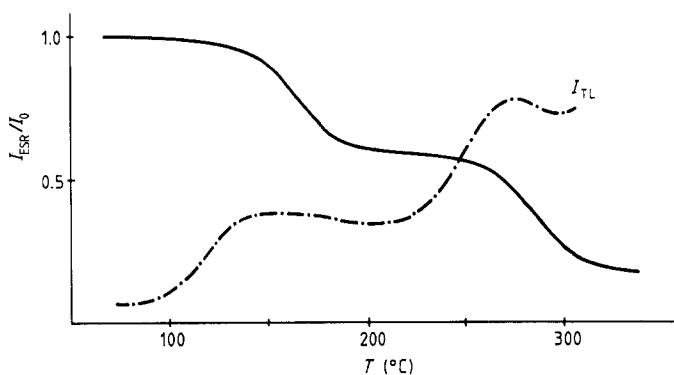
**Figure 6.** Step annealing curves of lithium diborate compounds. $I_0$ is the ESR signal intensity before the annealing steps. For the glow curve (indicated by the chain curve; arbitrary units) the heating rate was $10\,°C\,min^{-1}$. Dose: 4 Mrad.

In order to obtain a good enough signal-to-noise ratio for the ESR signals the samples were irradiated with doses of 1 and 4 Mrad. A weak ESR signal is observed after heating the samples for one hour or longer at 220 and 400 °C for sodium and lithium diborate respectively. This signal does not disappear at higher temperatures.

The samples were placed in a furnace and held at constant temperature for periods ranging from 1 to 60 min, at temperatures between room temperature and 220 °C and 400 °C for sodium and lithium diborate respectively. For periods longer than 10 min no appreciable change in the intensity of the ESR signal was observed. On account of this result, measurements of the ESR intensity were carried out on $\gamma$-irradiated samples before and after annealing treatments that lasted approximately 10 min. The ratios of the ESR signal intensities after and before annealing for sodium and lithium diborate are shown in figures 5 and 6 respectively. The ESR signal intensity was measured by taking the peak-to-peak distance of the ESR signal, because its shape did not change upon successive annealing treatments. For sodium diborate there are drastic changes in the signal intensities at about 145 and 175 °C, and for lithium diborate two changes are also observed at about 150 and 280 °C. These results support the assertion that two paramagnetic centres are being produced by irradiation. The intensity of the ESR signal did not change appreciably when measurements were carried out immediately upon irradiation and 40 days later. This result shows that the low-temperature peak cannot be correlated with the ESR centres. On account of this, in figures 5 and 6 the glow peaks of sodium and lithium diborate compounds recorded 40 days after irradiation are plotted together with the corresponding ESR signal intensity curves.

Keeping in mind that the value of $\beta_0$ corresponding to the step annealing procedure in this work was $2\,°C\,min^{-1}$, and that the heating rates used to obtain the glow curves were larger than $\beta_0$, the paramagnetic centres can only be connected to regions of the glow curve at temperatures higher than that corresponding to the maximum slope in figures 5 and 6. For lithium diborate the change in the ESR signal intensity with temperature at about 280 °C can only be connected with the peak at 280 °C, and the change at 150 °C with the peak at 170 °C and/or the peak at 280 °C. Because of the plateau in the curves showing ESR signal intensity against temperature it is unlikely that both paramagnetic centres are correlated to the same glow peak. Therefore we believe that one of the paramagnetic centres is related to the peak at 170 °C.

Straightforward analysis is not possible for sodium diborate, because the glow

curve consists of a broad peak. One of the paramagnetic centres can be related to thermoluminescent processes at temperatures above 145 °C and the other one to processes at temperatures above 175 °C. Again, because of the plateau in the ESR signal intensity curve we believe that the two paramagnetic centres are connected to different regions of the glow curve.

## 4. Conclusions

The results show that both sodium and lithium diborate compounds have a low-temperature peak, whose intensity decreases as the time between irradiation and recording of the glow curve increases. The ESR–TL correlation measurement indicates that the paramagnetic centres cannot be related to the low-temperature peak.

The experimental findings suggest that the two paramagnetic centres are related to two different glow peaks in the case of lithium diborate, and with the high-temperature region of the broad glow peak that is observed in sodium diborate 40 days after irradiation. As pointed out earlier, the ESR spectra obtained by us for sodium and lithium diborate compounds are similar to the spectra for alkali diborate glasses reported elsewhere [3], and not to the spectra of crystalline compounds. Analysis of the structure of the compounds by means of x-ray diffraction indicates that the compounds used in this work are amorphous. This result would account for the similarity of the spectra of our compounds to those of glasses. Similar results should be obtained with sodium and lithium diborate glasses.

## Acknowledgment

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